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Propellant Residues Deposition from Firing of 40-mm Grenades

Michael R. Walsh, Marianne E. Walsh, James W. Hug, Susan R. Bigl, Karen L. Foley, Arthur B. Gelvin, and Nancy M. Perron

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Cover photo: Firing of Mk19 40-mm machine from test firing point, 40/90 Range, Fort Richardson, Alaska, 22 February 2010 (Marianne E. Walsh, ERDC–CRREL).

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Abstract: Military live-fire training utilizes energetic materials that are never completely consumed. In February 2010, tests were conducted at Fort Richardson, Alaska, to determine the propellant residues deposition rates related to the firing of 40-mm grenades from an Mk19 machine gun. Two test pads were constructed, with 127 Mk281 (BA12) training rounds containing F15080 propellant (9.1% nitroglycerin-NG) fired over one and 144 M430 (B542) high-explosive rounds containing M2 propellant (19.5% NG) fired over the other. Replicate multi-increment samples were collected from the snow surface downrange of the firing positions in three sampling units on each pad. Samples were analyzed and results composited to derive an estimate of the unreacted energetics mass. The total estimated per-round deposition rate for the M430 high-explosive cartridge is 76 mg/round, 8.4% of the original NG load. The deposition rate for the Mk281 cartridge is 2.2 mg/round, 0.59% of the original NG load. Energetics deposition rates for the M430 rounds were between those for mortar projectiles and shoulder-fired rockets, which also utilize double-based propellants, are medium-velocity projectiles, and are fired from short-barreled guns. The Mk281 cartridges, with their NG-impregnated propellant grains, had a much lower NG deposition rate but a greater mass of unconsumed propellant.

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Preface

This study was conducted for the Department of Defense (DoD) Strategic Environmental Research and Development Program (SERDP) under the Environmental Restoration Program Project ER-1481. Dr. Andrea Leeson was the program manager.

This report was prepared by Michael R. Walsh and Arthur B. Gelvin, Engineering Resources Branch (ERB), at the U.S. Army Engineer Research and Development Center (ERDC), Cold Regions Research and Engineering Laboratory (CRREL), in Hanover, New Hampshire; Marianne E. Walsh, Susan R. Bigl, Karen L. Foley, and Nancy M. Perron, Biogeochemical Sciences Branch, CRREL; and James W. Hug, HTRW Engineering Section, Albuquerque District, Albuquerque, NM.

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1 Introduction

1.1 Background

The use of munitions during live-fire training is a necessary component for a well-trained military. The environmental impacts caused by the energetics associated with these munitions were not fully known until relatively recently. That knowledge was accelerated with the closure of ranges in Alaska (Eagle River Flats on Fort Richardson) and Massachusetts (Massachusetts Military Reservation) and subsequent research into the characterization of contaminants on those ranges (Racine et al. 1992; Clausen et al. 2004).

Initially, research emphasis was on the impact areas, where detonation of the projectiles had the potential to introduce large quantities of energetics into the environment. Characterization and deposition studies indicated that a properly functioning munition does not deposit appreciable amounts of energetics during training (Hewitt et al. 2005; Jenkins et al. 2006; Walsh, M.R. 2007). In the process of examining impact areas, the focus expanded to include the characterization of firing points (Walsh, M.E. et al 2001, 2007; Walsh, M.R. et al. 2005a, 2005b, 2007a).

The examination of firing points (FPs) as a source of energetic residues is a recent thrust in range sustainability research. Starting in 2000, studies funded by U.S. Army Alaska at Fort Wainwright's Donnelly Training Area (DTA) (Walsh, M.E. et al. 2001) indicated propellant-related energetic compounds were persisting at heavily used indirect-fire and direct-fire FPs. Further research in 2001 and 2002 (Walsh, M.E. et al. 2004) reinforced the original indications, with the propellant constituents nitroglycerin (NG) and 2,4-dinitrotoluene (DNT) recovered at several FPs. The State of Alaska lists DNT as a hazardous substance.

In 2002, the U.S. Department of Defense (DoD) Strategic Environmental Research and Development Program (SERDP) funded research at Fort Richardson, Alaska, to estimate high-explosives (HE) residue deposition (RDX, HMX, and TNT) from the live-fire detonation of 105-mm and 81-mm HE projectiles. Following the firing of the 105-mm howitzers, propellant residues containing DNT were collected from the snow-covered area in front of one of the guns (Walsh, M.E. et al. 2004). Results indicated

concentrations of energetic residues four orders of magnitude higher for the firing points than found at the impact areas (Hewitt et al. 2003; Walsh, M.R. et al. 2005b; Walsh, M.E. et al. 2007). When firing positions for shoulder-fired rockets were characterized, high concentrations of propellant residues were found in the surface soils (Thiboutot et al. 1998; Jenkins et al. 2006; Wingfors et al. 2006).

The ease of sample collection on snow and the straightforward processing of these samples led us to consider further investigations at winter firing points as an adjunct to the impact area research we were then conducting for SERDP. The methodology for the collection of samples on snow originally developed by Jenkins et al. (2000a, 2000b, 2002) was optimized by M.R. Walsh et al. (2005a, 2007b), making sampling much more efficient and repeatable.

Trials have been conducted on several common weapon systems including howitzers (M.R. Walsh et al. 2005b; Diaz et al. 2008), mortars (M.R. Walsh et al. 2005c, 2006), small arms (M.R. Walsh et al. 2007a; Brochu et al. 2009), rockets (Walsh 2009), and tanks (Ampleman in review). One common weapon system class for which no data had been collected is the medium caliber class, which includes 14.5- to 40-mm weapon systems. This report describes testing and results for one of these weapon systems, the Mk19 40-mm machine gun.

1.2 Objectives

The objectives of these tests were to derive an estimate of propellant residues generated as a result of live-fire training with the Mk19 40-mm machine gun using two different cartridges. Tests were conducted by firing both high-explosive rounds and training rounds. Propellants for these two types of cartridges differed in composition. The ultimate objective of this work is to provide data and results that can be used by the range community to assess the environmental impact of training with the Mk19. This information then can be used to develop an integrated training lands management plan.

1.3 Approach

Tests were conducted 22–23 February 2010 on the 40/90 range located on Fort Richardson, Alaska. Tests were conducted in winter to enable sample collections from an uncontaminated surface (snow) at an active range.

During the test, propellant residues from the firing are deposited on the snow surface downrange from the gun. These residues are visible, allowing demarcation of the area of deposition. The residues and underlying snow are collected using multi-increment sampling to estimate the total mass of energetic residues. The samples are then easily processed and analyzed. Because two tests were run, two areas within the firing point were required to prevent cross contamination. These firing positions were constructed on snow pads built for this purpose on the parking area of the range. No down-range sampling was conducted beyond the constructed pads because of the danger presented by the probable presence of unexploded ordnance below the snow cover and the sensitive nature of the fuzing on the 40-mm HE projectiles. Each round contains only about 4 g of propellant, so a large number of cartridges (>100) were fired to ensure adequate residues for the analyses.

2 Field Sampling Methodology

2.1 Field site and conditions

No live-fire training had occurred at the Fort Richardson 40/90 Range during the winter immediately prior to our test. The parking area at the firing point had been plowed, leaving little snow cover in the areas where the firing positions were to be set up (Figure 1). We delineated test areas and transferred snow from the area behind the firing positions to construct snow pads for our tests (Figure 2). Forward of the firing positions, the area was flat for 15 m before encountering the opposite edge of the parking area. The snow bank on the down-range side was removed by Range Control to facilitate firing the weapon system. The temperature at the time of testing was around –4 °C with variable northern winds around 1 m/sec. The sky was partially overcast under a weak sun at the start of testing but skies cleared as the day progressed. Undisturbed snow depth was less than 60 cm on either side of the parking area.

Figure 1. 40/90 Range firing point parking area prior to pad construction.

Figure 2. Test pad for first firing from downrange; gun is at left of image.

The two snow pads measured approximately 11.5-m long and 7.5-m wide for the first test and 13.5-m long by 8.2-m wide for the second test (Figure 3). Pad depth was variable, with a target depth of 20 cm. A 5-cm top layer was added to a 15-cm base layer to serve as a sampling surface. The pads were separated by about 4 m. The second pad was built following the conclusion of the first test to prevent cross-contamination between tests.

To determine if any pre-existing residues occurred in the area, baseline samples were taken from both the snow mine used to construct the pads as well as areas adjacent to the range. Snow mine samples were taken at mid snow depth for use as the pad base layers and from the surface, for use as the top layer for the pads. Baseline samples were obtained at three locations away from the firing pads on 22–23 February. The unusually mild weather allowed efficient operations to occur, and no delays in site preparation were encountered. The pads, snow mines, and baseline sample locations were recorded using a Trimble GPS Pathfinder Pro XR system (±1 m) and supplemented with hand measurements taken with a tape measure.

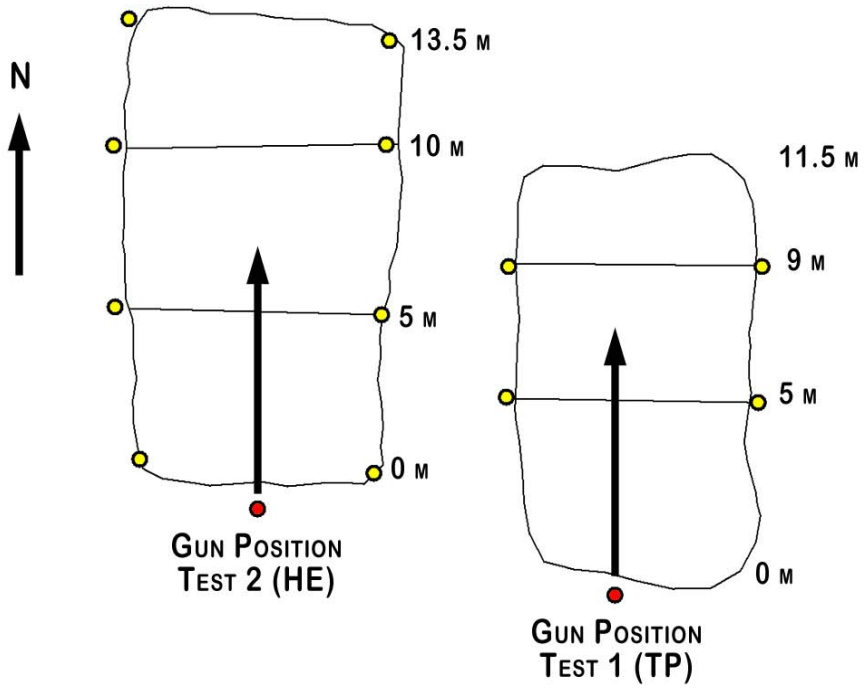


Figure 3. Test pad layouts.

2.2 Munitions tested

The munitions tested were the Mk281 MOD 0 training and practice (TP) round and the M430 high explosive (HE) round (Table 1). The M430 HE round contains 4,000 mg of M2 double-based propellant, a standard U.S. military propellant formulation, with nitrocellulose (NC) and nitroglycerin (NG) as the energetic constituents (U.S. Army 1994). The Mk281 TP round can contain any one of several types of propellants, depending on the lot. For the lot used in our tests, the propellant specified was 4,040 mg of F15080, a European-manufactured[1] NG-impregnated double-based propellant with NC, NG, EC (Ethyl Centralite), and Akardite II as the major constituents. The F15080 propellant is quite different from previously tested propellants in that the NG resides on the surface of the propellant grains rather than being a component of the NC matrix that makes up the bulk of the propellant grain. We hypothesize that these physical and chemical characteristics had a major effect on the resulting NG deposition rate for our test utilizing this propellant compound. Detailed information on the munitions and propellant constituents can be found in Appendix A.

[1] Manufacturer is Nitrochemie of Wimmis, Switzerland.

Table 1. Propellant constituents analyzed for firing point test.

Weapon System	Munition (Mil / DODIC)	Propellant	Constituent	Constituent Load (mg/% of total load)
40 mm Mk19 MOD 3 Grenade Machine Gun	Mk281 MOD 0 / BA12 (TP)	F15080*	NG	370 / 9.1%
	M430 / B542 (High Explosive)	M2	NG	900 / 19.44%

*From ammunition data card for a different lot number. Data for both munitions from Nitrochemie and DAC.

2.3 Firing of munitions

Live-fire testing of the 40-mm weapon system occurred in two stages (Figure 4). On 22 February, 127 Mk281 TP rounds were fired from the first firing position. One round jammed on loading and was not fired. On 23 February, 144 M430 HE rounds were fired from the second firing position. The cartridges, which were assembled onto a metal belt for automatic fire, were fired in up to 5-round bursts until all ammunition was expended. Sampling commenced after the area was cleared by our unexploded ordnance technician.

Figure 4. Firing of M430 HE grenades over test pad.

2.4 Sampling method

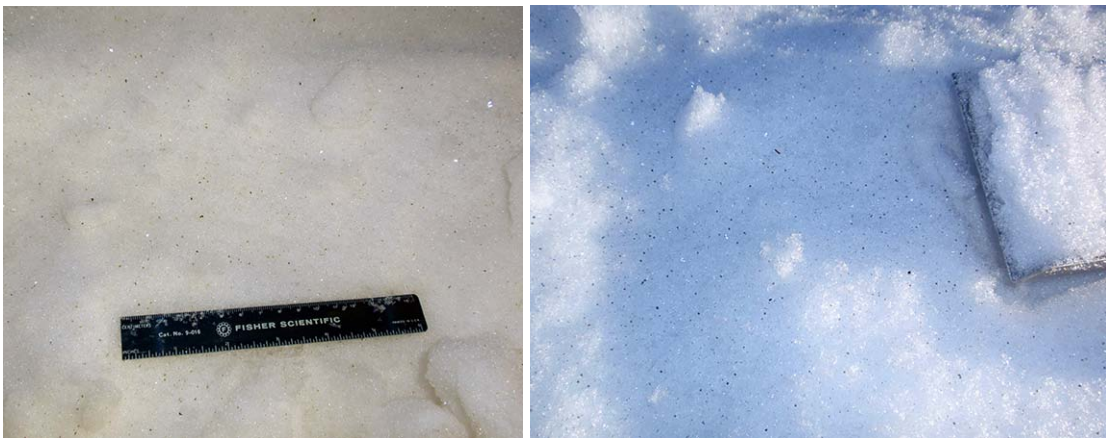
The post-firing propellant residues sampling was done from the surface of the two test pads following the multi-increment sampling (MIS) protocol established by M.R. Walsh et al. (2007b). Briefly, a representative sample composed of 40-48 increments of surface snow and residues was collected with a flat-bottomed hand scoop to make up a single sample within a sampling unit (SU). Use of MIS allowed us to test and compensate for uncertainty derived from the small total area collected from within each SU, typically less than 1 m^2.

The pads were divided into three SUs along the down-range axis (Table 2; Figure 3). In each SU, three multi-increment (MI) samples were taken by using a 10- x 10- x 2.5-cm polytetraflouroethylene (PTFE)-coated scoop. Increments were placed in a laboratory-grade clean polyethylene (PE) bag. When done sampling, the bag was labeled, a tag labeled and attached to the bag, the bag sealed with a tie-wrap, the sample recorded in a log book, and the sample placed in a shaded location until transportation back to the processing laboratory located nearby on post.

Table 2. Sampling unit areas, February 2010.

Sampling Unit	Area (m^2)	Percent of Pad Area
Pad #1 (TP Rounds) – 0-5 m	36	42%
Pad #1 (TP Rounds) – 5-9 m	29	34%
Pad #1 (TP Rounds) – 9-11.5 m	21	24%
Pad #2 (HE Rounds) – 0-5 m	38	34%
Pad #2 (HE Rounds) – 5-10 m	41	37%
Pad #2 (HE Rounds) – 10-13.5 m	32	29%

In addition, we obtained one surface MI sample in the 0- to 5-m SU of each pad by using a 20- x 20- x 2-cm scoop. These samples were difficult to obtain because of the traffic in the area incurred during the taking of the triplicate samples. Very little area was available for sampling, and what area was available was not evenly distributed throughout the SU. No subsurface samples were obtained because the muzzle blast of the weapon was insufficient to cause mixing of the surface snow. A visual inspection of propellant debris on the pad surfaces (Figure 5) indicated the debris was contained on the pads, which obviated the need to sample off the pads.



a) F15080 Propellant debris (TP) b) M2 Propellant debris (HE)

Figure 5. Propellant debris on test pad surfaces after tests.

Trays were placed in front of the gun's muzzle during both tests to collect a small amount of residues for microscopic analysis for another project as well as the chemical analyses for this project (Figure 6). These trays were removed partway through both tests to minimize the impact on the mass deposition tests covered in this report.

Figure 6. Location of trays used to collect propellant debris.

3 Sample Processing and Analysis

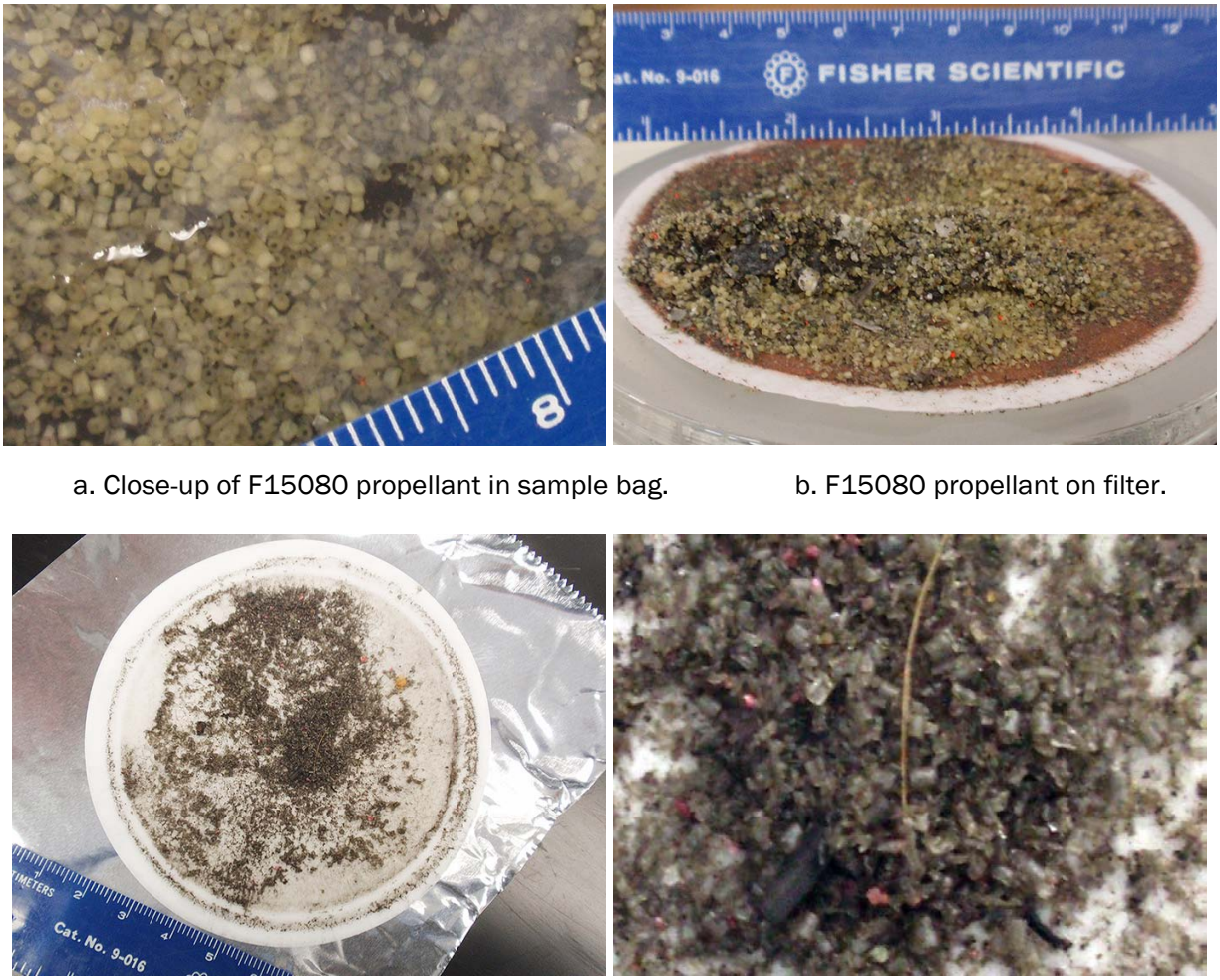
3.1 Snow samples

The samples of snow were transferred to a laboratory at the Fort Richardson cantonment area for processing. Upon arrival, the samples were transferred from the field bags to clean bags, double-bagged, and placed in clean PE tubs for thawing (Figure 7). Placing the samples in clean bags reduces the chances of cross-contamination from contact with adjoining bags and residues on the exterior of the sample bags. The use of double-bagging and tubs was necessary because of the inclusion of sharp pieces of debris collected with the snow samples. Otherwise, debris from the firing of the rounds could pierce the sample bags and allow the thawed samples to leak.

Figure 7. Samples in tubs at thaw location.

Samples were shifted from warmer to cooler areas of the lab's logistics bay to prevent over-warming (temperatures >4 °C) after melting. The samples were then processed based on completion of melting and the sample area they were taken from. Samples anticipated to have the least residues were

processed first and those anticipated to be more contaminated were done last to reduce the possibility of cross-contamination (Figure 8).



a. Close-up of F15080 propellant in sample bag.

b. F15080 propellant on filter.

c. M2 propellant on filter.

d. Close-up of M2 propellant.

Figure 8. Propellant residues during initial processing of 0-5 m SU samples.

Processing involved filtering the melted samples using a vacuum system to separate the solid fraction from the aqueous fraction (Figure 9). The solid fraction was collected on filter papers[1]. Following filtering, the papers were placed in a clean amber jar, air dried, and stored in a refrigerator at <4°C. The volume of the aqueous fraction was recorded prior to mixing and decanting of two or four 500-mL aliquots into glass amber bottles. (Two bottles were the normal number collected for analyses; four were collected for a laboratory quality assurance procedure.)

[1] Whatman glass microfiber 90 mm ∅ grade GF/A

One (or three) 500-mL aliquot of the filtrate was pre-concentrated by passing it through a Waters Porpak RDX[1] solid-phase extraction (SPE) cartridge and eluted with 5 mL of acetonitrile (AcN), resulting in a 100:1 concentration of the analytes (Walsh and Ranney 1998). The concentrate was split into two aliquots, 3.5 mL for analysis and 1.5 mL for archiving. When processing was completed, the 3.5-mL splits and the filters were shipped to the CRREL's analytical chemistry laboratory in Hanover, New Hampshire, for final processing and analysis.

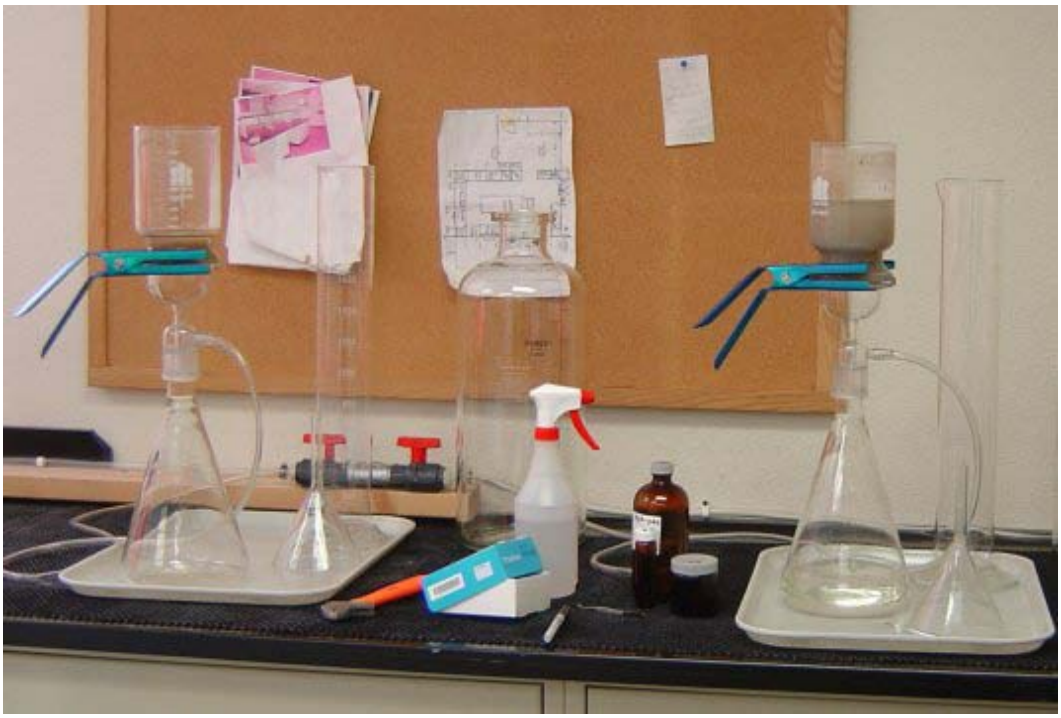


Figure 9. Sample filtration setup at the processing laboratory on post.

Prior to final processing, the air-dried filters were weighed. Subtracting out the weight of the filter gave us the weight of the firing point debris. This debris consisted of whole and partial propellant grains, propellant residues, debris from the firing of the cartridges (metal fragments from the rotating bands, parts of the obturator rings, etc.), and whatever other solid contaminants may be in the sampling snow matrix. Separation and analysis of these components will give us a good estimate of the total propellant components resulting from the firing of the rounds.

The NG was extracted from the solids on the filters by shaking for 18 hours with AcN. The AcN extracts from the solid phase extraction of the melted

[1] Sep-Pak, 6-cm^3, 500-mg

snow and of the solid residue on the filters were analyzed by high-performance liquid chromatography (HPLC). Analyte concentrations were determined following the general procedures of SW 846 Method 8330B to determine nitroaromatics, nitrate esters, and nitramines by HPLC (USEPA 2006). The HPLC method has an analytical error that is very small, about 2% relative standard deviation (RSD) for replicate injections.

Prior to analysis, each extract was diluted with AcN based on the intensity of the color from the EXPRAY test (Walsh, Walsh, and Hewitt 2010) so that the injected concentration would be less than 10 mg/L. The AcN was then mixed with reagent-grade water (1:3 v/v) and filtered through a Millex-FH filter unit[1]. Determinations were made on a modular system[2] composed of a Finnigan SpectraSYSTEM Model P4000 pump, a Finnigan SpectraSYSTEM UV2000 dual wavelength ultraviolet/visible absorbance detector set at 210 and 254 nm (cell path 1 cm), and a Finnigan SpectraSYSTEM AS300 autosampler. Samples were introduced with a 100-µL sample loop. Separations were achieved on a 15 cm x 3.9 mm (4 µm) NovaPak C8 column[3] at 28 °C and eluted with 1.4 mL/min of 15:85 isopropanol/water (v/v) Under these conditions, NG eluted at 8.7 minutes and Akardite II® eluted at 9.7 minutes.

Energetics calibration standards were prepared from analytical reference materials obtained from Restek Corporation (Bellefonte, PA). The analytical reference materials were 8095 Calibration Mix A (1 mg/mL) and a single-component solution of NG (1 mg/mL). A spike solution at 1 mg/L was prepared from 8095A Calibration Mix and the single-component solution of NG. Spiked water samples at 0.002 mg/L were prepared by mixing 1.0 mL of the spike solution to 500 mL of water in a volumetric flask. Following SPE, the extract target concentration was 0.20 mg/L for each analyte. Reference material for Akardite II (3-methyl-1, 1-diphennylurea) was obtained[4]. It was used to prepare a calibration standard at 20 mg/L in AcN.

To calculate the mass of the unreacted analyte in the residues deposited on the snow, we first had to derive an estimate of the mass in the two fractions. For the soot fraction, the extract concentration (mg/L) is multiplied

[1] Millipore, PTFE, 0.45 µm

[2] Thermo Electron Corporation of Waltham, MA

[3] Waters Chromatography Division of Milford, MA

[44] Sigma-Aldrich

by the volume of AcN used in the extraction (L). For the aqueous fraction, the extract concentration is multiplied by the volume of water from the snow melt. These masses were then divided by the actual area sampled with the scoops (m^2) to derive the surface concentrations in mg/m^2. This value was multiplied by the measured area of the SU to derive our estimates of the mass within the area sampled (mg) (Jenkins et al. 2002; Hewitt et al. 2003). For the HPLC, the detection limit was 0.05 mg/L for NG in the AcN extract. Values below this limit are labeled as "ND" in the data, indicating "no detectable" analyte.

3.2 Quality control procedures

Quality control (QC) procedures were conducted both in the field and in the laboratory. Field QC, noted previously, included replicate sampling within the residue plumes, background samples, and snow mine samples. In the processing laboratory, blank samples consisting of filtered water from a reagent water filtration system were periodically run through a filter assembly and SPE setup for later analysis at the laboratory. This procedure was designed to determine whether cross-contamination from the sample filtering apparatus was occurring. Water fractions for several samples were divided into three aliquots and run through the SPE to determine whether recovery rates from the SPE procedure were consistent. SPE spikes were run to determine cartridge filter retention and recovery. These processes are described in greater detail in M.R. Walsh (2007). Two samples were taken in February to determine the background concentration of the analyte in the areas to be sampled prior to the test. Two baseline samples were taken from the snow mine areas used as sources for the test pads. These mines were adjacent to the test pads and thus more likely to contain energetics from training at this site. Surface and subsurface samples were taken and analyzed for NG.

Initially, we did not know the composition or chemical compound distribution of the TP propellant grains. Analyses of the results for these rounds indicated a need to further investigate the propellant residues captured on the filters during processing. The normal procedure for processing of the filters, which we followed, is to weigh the filters and solids after drying and prior to dissolution of the propellant. Following propellant dissolution and sampling for the analytical chemistry, the filters and remaining debris are returned to refrigerated storage.

The filters for the most heavily loaded sampling units were taken out of refrigerated storage and washed with acetone in a glass dish. The solids were gathered in a pre-weighed weight boat, allowed to dry in a fume hood for one hour, and reweighed to derive the mass of solid non-propellant debris. This data enabled a more accurate estimation of the original propellant and propellant residues on the filters, allowing us to refine our NG recovery estimates. We also determined the NG content of several propellant grains recovered from sample trays placed in front of the gun firing the TP rounds. The results for these tests still looked low in comparison to the amount of solids on the filters for the TP rounds, leading to the need to further investigate the propellant (refer to "Discussion," Section 5).

4 Results

The background samples collected from the area surrounding the firing position and the baseline samples collected from the snow mines contained no detectable NG, indicating a clean test area.

4.1 Deposition rate

A total of 20 MIS, composed of 833 increments over a combined area of 200 m^2 in six sampling units, were taken to determine the deposition and distribution of NG from the firing of 127 TP and 144 HE 40-mm rounds during the two tests conducted. The test pads over which the firing occurred were divided into three SUs each, ranging in size from 21 m^2 to 41 m^2 (Figure 3). No subsurface samples were obtained and sampling outside the pad areas did not occur except for background samples and baseline samples at the snow mines used to construct the test pads.

A summary of the analytical data averaged for the replicate samples are given below in Table 3 (see also Appendix B). The estimated average mass values do not include the 20-cm scoop samples in the 0-5 m areas (refer to "Discussion," Section 5). The average mass of NG per round for the TP rounds is 270 mg/127 rounds or 2.1 mg/round and for the HE rounds the average is 11,000 mg/144 rounds or 76 mg/round. The largest estimated average mass of NG lies within the first 5 m down-range of the firing position, with the remaining areas containing an order of magnitude less additional NG. For Pad 1 (TP), 92% of the estimated total NG was in the 0- to 5-m SU (42% of total pad area), 7.8% in the 5- to 9-m SU (34% of pad area), and 0.058% in the 9- to 11.5-m SU (24% of pad area). For Pad 2 (HE), 98% of the estimated total NG was in the first 5 m (34% of pad area), 1.7% in the 5- to 10-m SU (37% of pad area), and 0.04% in the downrange transect (29% of pad area). Although the SUs are not equal in area, looking at the NG deposition rates based on mass per unit area shows that in the 0- to 5-m SU, deposition rates are 7.2 and 260 mg/m^2 for the TP and HE pads respectively, 0.76 and 4.1 mg/m^2 for the center SU, and 7.6 x 10^{-3} and 0.13 mg/m^2 for the downrange SU. Three points are not sufficient to derive a formula for the gradient, but the data indicate a power relationship with distance from the firing position.

The solids masses on the filters from the 0- to 5-m SUs were substantial, so we weighed them (Table 4). The mass of solids recovered from the 0- to 5-m SUs of the two pads differed substantially. The following masses are normalized to a sampled area of 0.40 m². For the TP rounds, 1.6g of residues on average was filtered from each sample. For the HE rounds, 0.77g of solid residues was filtered from each sample. Thus, Pad 2 (HE) yielded 44% as much solid residues as Pad 1 (TP). We weighed the remaining debris on the filters following solvent extraction of the filters to obtain the mass of the insoluble debris. For the three filters from the triplicate samples taken from Pad 1 (TP), the insoluble debris weighed 0.78, 0.55, and 0.55 g. There was very little insoluble debris remaining on the Pad 2 (HE) filters. We weighed only the debris from the median-weight filter. This filter contained only 0.12 g of material.

Table 3. NG residue mass for test sampling units.

Sampling Unit (SU)*	SU Area (m²)	Sampled Area† (m²)	Replicates	Est. Avg. Mass NG (mg)	NG Mass in SU
Pad 1 (40-mm TP Rounds)					
0 to 5 m*	36	0.40 (1.1%)	3	250	92%
0 to 5 m**	36	1.5 (4.2%)	1	290	—
5 to 9 m	29	0.40 (1.4%)	3	22	7.9%
9 to 11.5 m	21	0.40 (1.9%)	3	0.16	0.06%
Total for Pad 1	**87**	**5.1 (5.9%)**		**270**	**—**
Pad 2 (40-mm HE Rounds)					
0 to 5 m	38	0.41 (1.1%)	3	11,000	98%
0 to 5 m**	38	1.9 (5.0%)	1	7,000	—
5 to 10 m	41	0.48 (1.2%)	3	170	1.5%
10 to 13.5 m	32	0.40 (1.2%)	3	4.1	0.04%
Total for Pad 2	**110**	**5.8 (5.3%)**		**11,000**	**—**

*Distance from Firing Position

** Taken with 20-cm scoop; not counted in averages.

† Average sampled area of replicates; (percentage) is of sampling unit area sampled.

Table 4. Filter mass components.

Sample	Total Mass on Filter (g)	Mass of Debris* on Filter (g)	Propellant Mass on Filter (g)	Percentage Propellant on Filter	Percentage Debris on Filter
Pad 1 (40-mm TP Rounds)					
0 to 5 m Rep 1	1.9	0.78	1.1	58%	42%
0 to 5 m Rep 2	1.5	0.55	0.94	63%	37%
0 to 5 m Rep 3	1.5	0.55	0.98	64%	36%
Average Values	1.6	0.63	1.0	62%	38%
Pad 2 (40-mm HE Rounds)					
0 to 5 m Rep 2	0.77	0.12	0.65	84%	16%

*Insoluble debris remaining after solvent extraction process

The original NG loads for the TP and HE munitions are 370 mg and 900 mg, respectively. The calculated propellant residue deposition rate for NG is 8.4% (76/900) of the original propellant NG load for the HE rounds (M2 propellant) and 0.59% (2.2/370) of the original NG load for the propellant for the TP rounds (F15080 propellant). The NG percentage value for the TP rounds was very low compare to the results of past experience and the results of analysis of the HE round residues, but it agrees well with the NG analyses of propellant grains recovered from trays placed in front of the gun muzzle for the TP firing test. We also analyzed the TP firing point residues for Akardite II, a component of the F15080 propellant, to verify the mass quantities we were estimating. Approximately 950 mg of Akardite II were estimated to have been deposited from the residues recovered from the 0- to 5-m section of the test pad and 80 mg from the 5- to 9-m section of the pad (Appendix B). These values correspond to a concentration of 9.1%, within range of the propellant formulation. From this, we can conclude that that the mass of residues estimated for the tests are valid (see Section 5).

Quality control procedures were conducted to verify the procedures and supplies used to obtain the results of our analyses. Laboratory and process control spikes and blanks were analyzed and the data indicates these processes did not contribute significant error to the results. Neither of the filtered water blanks processed at the field lab contained detectable levels of NG. Four solid phase extraction blanks were run using fresh Waters Porpak RDX cartridges and filtered water. When eluted, no NG was detected in the filtrate, indicating no analyte contamination in the process. Lab control spikes (0.002 mg/L) indicated a recover rate of 90–95% for three runs.

5 Discussion

The estimated NG deposition rates for the TP and HE rounds tested were 0.59% and 8.4% of the original propellant loads, respectively. In developing these estimates, we did not use the 20-cm scoop samples from the 0- to 5-m SUs because of the difficulty in sampling in a systematic manner in the areas. The triplicate samples taken with the 10-cm scoops had very good agreement in the 0- to 5-m SUs, where 92% to 98% of the residual NG was recovered (Table 3 and Table B2). In these areas, the RSD for the replicate MIS data is 2.0% for the TP rounds and 5.4% for the HE rounds. In other areas where the deposition rate is not as high, the RSD varies from 2.7% to 54%, the highest being in the farthest down-range SU for the TP test. This area contained less than 0.1% of the total residues for that test.

The disparity between the NG deposition masses for the TP and the HE rounds warranted further investigation. Although the firing of the TP rounds generated more solid residues, the NG deposition rate estimate was significantly lower. Our experience has been that residues typically reflect the chemical composition of the original propellants. A significant difference in NG concentration of the residues thus indicated two different propellants. This is in conflict with the U.S. Army training manual (TM), which states that the propellants for the two different rounds are both the same—M2 (U.S. Army 1994). This TM was our original source of information on propellant types for the rounds.

The first indication that the propellants for the two munitions actually differed was the physical appearance of the unconsumed grains recovered from the samples. The size, color, and quantities of the residues were all clearly different. The solid residues on the filters from the three samples taken in the 0- to 5-m SUs with the 10-cm scoops were analyzed for NG (Table 4). Initially, we hypothesized that the solids on the filters were composed of 85% propellant residues and 15% insoluble debris. Much less NG was recovered from the residues of the TP rounds than from the residues from the HE rounds. The initial results from the analyses of the HE propellant residues were within the range of the published specification on M2 propellant if the mass of solid residues is around 85% propellant. The analytical method seemed to be functioning, so we continued to look into

the TP propellant because it did not appear to be the M2 propellant specified in the TM.

A check of the ammunition lot numbers and ammunition data cards showed that the propellants were not the same for the two types of cartridges. The HE rounds contained the standard M2 propellant, while the TP rounds contained the Swiss-manufactured F15080 propellant (Haeselich, Kelly, and Miller 2006). The specifications for the F15080 propellant, given in the European Community Safety Data Sheet (Moor 2006) indicated an NG content of 8%–12%, about half that of M2 propellant's 18.5%–20.5% NG content (U.S. Army 2005). Even after taking the lower NG content into account, the estimated residual mass of NG for the TP propellant was still much lower than expected.

Being unfamiliar with this propellant formulation, we felt it was necessary to analyze some of the propellant grains to determine their actual NG content. Ten mostly intact grains were recovered from one of the trays placed in front of the firing position for the TP test. These grains were weighed collectively (5.2 mg), dissolved in 10 mL of acetonitrile, and two replicates analyzed for NG. A total of 0.025 mg was recovered, corresponding to approximately 0.6% of the original propellant mass. There still existed a disconnect between what we were seeing in the laboratory (≈0.6%) and what the specification for the propellant stated (9.1%). As a result of our observations, we looked further into the propellant's formulation and manufacture.

The F15080 propellant is classified as a double-based propellant in some literature and as a single-base extruded propellant with NG impregnation (EI® propellant) in others. The NG resides on the surfaces of the grains, penetrating partway into the grains at the outside surfaces and along the perforations (Kelly 2010; Figure 10). The propellant burns at around 3000 °K (2700 °C). We hypothesize that the presence of most of the NG on the surface of the grains, the high burning temperature of the propellant, and the highly labile nature of NG will result in more complete consumption of NG than if it were thoroughly embedded within the NC matrix of the grains, as with M2 propellant. In other words, it behaves like a single-based propellant with a surface matrix diffused with readily-available NG.

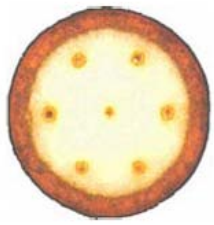


Figure 10. Cross-section of EI propellant grain (Elmasri et al. 2008).

Our test data indicate that a much lower percentage of the original NG remains in the residues of the 40-mm TP round than in the residues of the HE rounds. However, from our analysis of the mass of propellant and propellant residues following firing, much more of the propellant remains after firing TP rounds than HE rounds. Based on our investigations into the physical characteristics of the propellant grains, this is expected, as the TP propellant consists of multi-perforated grains that are known to be inefficiently consumed (US Army 1984). However, the TP residue is mostly NC, which has not been found to be a problem in the environment. We have little information on the Akardite II, a stabilizer component of the propellant (<2%), other than it has very low water solubility. This low solubility combined with the stability of the NC matrix within which it is embedded and the low mass present within the propellant leads us to hypothesize that it will not be a concern to the environment. The toxicity of the compound is not known, however, and a final determination of its impact on training ranges cannot be known at his time.

We used the 0- to 5-m SU results to estimate the amount of propellant residue deposited from firing the two munitions. For the HE rounds, an average of 0.65 g of propellant was contained in the 0.42-m^2 samples. Extrapolated over the 38-m^2 SU, we estimated about 60 g of propellant after firing 144 rounds. This correlates well with the 8.4% recovered NG for the M2 propellant. For the TP rounds, the corresponding estimate was over 90 g of propellant from firing 127 rounds. Extrapolated over the whole test pad, this is over 19% of the original F15080 propellant load for the round, which does not correlate well with the NG residues for this round. Because the NG resides on the surface, the single-base core of the propellant grain is what mostly remains in the residues. A better confirmatory indicator for the F15080 residue mass is the stabilizing compound Akardite II, found throughout the propellant. The mass of Akardite II found in the propellant grains recovered from the tray in front of the gun was 0.060 mg, 1.1% of the total mass (5.2 g) of the grains. The specification calls for 0.9% to 1.2%.

For the 0- to 5-m area for the TP tests, a mean of 9.1 mg of Akardite II was recovered from a mean of 1 g of unconsumed propellant, corresponding to a concentration of 9.1% in the propellant residues, again within specifications. The total estimated mass of Akardite II deposited on the test pad was a little over 1 g, which corresponds to 19% of the initial mass contained in the cartridges fired for the test. This agrees well with the rate derived from the sample mass calculations above.

We have found in the past that weapon systems that have longer barrels, rifled barrels, or larger propellant loads generally have a lower percentage of their propellant deposited as residues. This is likely due to the higher temperatures and pressures generated in these types of armaments. By contrast, short-barreled guns, such as mortars and the Mk19, are likely to have higher residues mass deposition rates. The Mk19 machine gun firing the 40-mm HE grenade cartridge is not a clean firing weapon system. Table 5 summarizes the results of testing we have done with the Mk19, man-portable rockets, mortars, howitzers, a tank, and small arms. The data are presented in rough order of the percent of the analyte not consumed per round fired. The 40-mm HE grenades rank near the top.

Table 5. Comparison of various firing point analyte loads.

Weapon System	Propellant	Analyte	Analyte / Round (g)	Residues*/ Round (mg)	Residues*/ Original Load
Shoulder-fired Rockets					
84-mm Carl Gustav[3]	AKB 204	NG	140	20,000	14%
66-mm LAW[4]	M7	NG	22	42	0.1%
84-mm AT	AKB 204	NG	130	95,000	73%
Medium-caliber Weapon Systems					
40-mm (HEDP)	M2	NG	0.90	76	8.4%
40-mm (TP)	F15080	NG	0.37	2.2	0.59%
Mortars					
81-mm	M9	NG	30	1,000	3.5%
120-mm	M45	NG	26	350	1.4%
Small Arms					
5.56-mm Rifle	WC844	NG	0.16	1.8	1.10%
5.56-mm MG[1]	WC844	NG	0.16	1.3	0.79%
7.62-mm MG	WC846	NG & DNT	0.27	1.5	0.56%

Weapon System	Propellant	Analyte	Analyte / Round (g)	Residues*/ Round (mg)	Residues*/ Original Load
9-mm Pistol	WPR289	NG	0.040	2.1	5.44%
12.7-mm MG[1]	WC860 & WC857	NG	1.5	11.	0.73%
Leopard Tank[2]					
105-mm (MIS)	M1	DNT	300	6.7	2.2×10^{-3}%
105-mm (Trays)	M1	DNT	300	7.8	2.7×10^{-3}%
Howitzers					
105-mm	M1-I & II	DNT	42	34	8×10^{-2} %
155-mm	M1	DNT	275	1.2	5×10^{-4} %

* Analyte residues (Estimated)

[1] Average loads and residues from ball and tracer rounds in linked ammunition.

[2] Preliminary results. (Ampleman et al. in review)

[3] Thiboutot et al. (2008a)

[4] Thiboutot et al. (2008b)

What are the implications of this research for the range manager or the soldier on the training range? For every 100 TP rounds fired, over 60 g of NC will be deposited less than 5 m from the barrel of Mk19 gun. This is more propellant than is contained in 17 live rounds. For a vehicle-mounted weapon system, this may become a serious fire hazard. On a heavily-used fixed-position firing range, the same hazard may be present.

A laboratory test conducted by Dr. Susan Taylor is underway at CRREL to determine the environmental leaching rate of NG from propellant residues as collected from the trays in front of the gun positions during the firing point tests for the study reported here. Past experience indicates that NG leaches readily from surfaces and from the edges of NC-based propellant residues. When these surfaces are depleted, the leaching rate slows significantly, and NG may remain within the NC propellant matrix for over 30 years. For small-volume propellant residues such as from the 40-mm tests, most NG will likely leach out quickly because of the high surface-to-volume ratio and the presence of many edges. If the NG remains stable within the residues, there will eventually be a range hazard. If it leaches out, there will be a groundwater contamination problem. Either case warrants attention from the range community.

6 Conclusions

Training with the Mk19 machine gun using the M430 40-mm HE cartridge will result in moderate deposition and accumulation of nitroglycerin-containing residues in the first 5 m in front of the firing position. Our tests indicated that about 8% of the propellant and NG are not consumed during firing of the weapon. The Mk281 40-mm TP cartridge leaves more unconsumed propellant, but significantly less NG (0.59% of the bulk mass) at the firing position due to the presence of the NG on the propellant grain surface. On 40-mm ranges with fixed firing positions, the propellant residues from both types of rounds may build up to hazardous levels over time, an issue that will have to be addressed by range managers. Furthermore, leaching of NG from the unburned propellant may cause a groundwater contamination problem. For mounted weapon systems, the presence of the propellant residues may constitute a fire hazard.

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Acronyms and Abbreviations

Term	Spellout
AcN	acetonitrile
AT	anti-tank
C4	an explosive material composed of 91% RDX, 9% oil
Composition B	an explosive material composed of 60% RDX, 39% TNT, 1% wax
CRREL	Cold Regions Research and Engineering Laboratory
DNT	Dinitrotoluene (2,4-dinitrotoluene), an explosive compound
DoD	U.S. Department of Defense
DODIC	Department of Defense Identification Code
DRDC	Defence Research and Development Canada
EC	ethyl centralite
EI®	Extruded – Impregnated
EOD	Explosive Ordnance Disposal
ER	Environmental Restoration
ERDC	Engineering Research and Development Center
FP	firing point
GMG	grenade machine gun
GPS	global positioning system
HE	high explosive
HEDP	high-explosive / dual-purpose
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, an explosive compound
HPLC	high-performance liquid chromatography
LAW	light anti-tank weapon
LCS	laboratory control spike; laboratory control sample
MG	machine gun
MI	multi-increment
MIDAS	Munitions Items Disposition Action System
MIS	multi-increment sample
MMR	Massachusetts Military Reservation
MMRP	Military Munitions Response Program
MS	matrix spike
MSD	matrix spike duplicate

Term	Spellout
NC	nitrocellulose, an energetic compound
NG	nitroglycerin, an energetic compound
QA	quality assurance
QC	quality control
RSD	relative standard deviation
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine, an explosive compound
SERDP	Strategic Environmental Research and Development Program
SPE	solid-phase extraction
SU	sampling units
TNT	2,4,6-Trinitrotoluene, an explosive compound
TP	training / practice
USACE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency
UXO	unexploded ordnance

Appendix A: Munitions Data

Table A-1 contains information relevant to the munitions used during the test covered in this report. Images of the ammunition cans from the tests are shown in Figures A-1 and A-2. Information displayed on the cans includes national stock number (NSN) Department of Defense Identification Code (DODIC), military designation, and lot number. Propellant loads for the analytes of concern are given in Table 1 (of the main text). Table A-2 gives more detailed information on the propellants for each type of munition.

Table A-1. Munitions data.

NSN	DODIC	Nomenclature	Lot No.	Drawn for tests
1310-01-472-9871	BA12	Cartridge, 40 Millimeter: Practice, Mk281 Mod 0	NPG08L003-055	128
1310-01-159-8043	B542	Cartridge, 40 Millimeter: HEDP, M430	MA-88G023Y033F	144

Note: Munitions were drawn from inventory, Ammunition Supply Point, Ft. Richardson, AK.
Source: US Army (1994).

Table A-2. Propellant data.

DODIC	Propellant	Mass of Propellant (g)	Mass (mg) / Percentage NG	Other Major Constituents
BA12	F15080	4.04	370 / 9.1%	NC: 88% Akardite II: 1.2% Ethyl Centralite: 0.2% KSO_4: 0.65%
B542	M2	4.64	900 / 19.44%	NC: 77.5% K Nitrate, 0.75% Ba Nitrate: 1.4% Ethyl Centralite: 0.60% C (Graphite): 0.30%

Sources: F15080 (BA12): Moore (2006); B. Vogelsanger (e-mail communication); M2 (B542): US Army (2005)

Figure A-1. Ammunition box for TP rounds used during test.

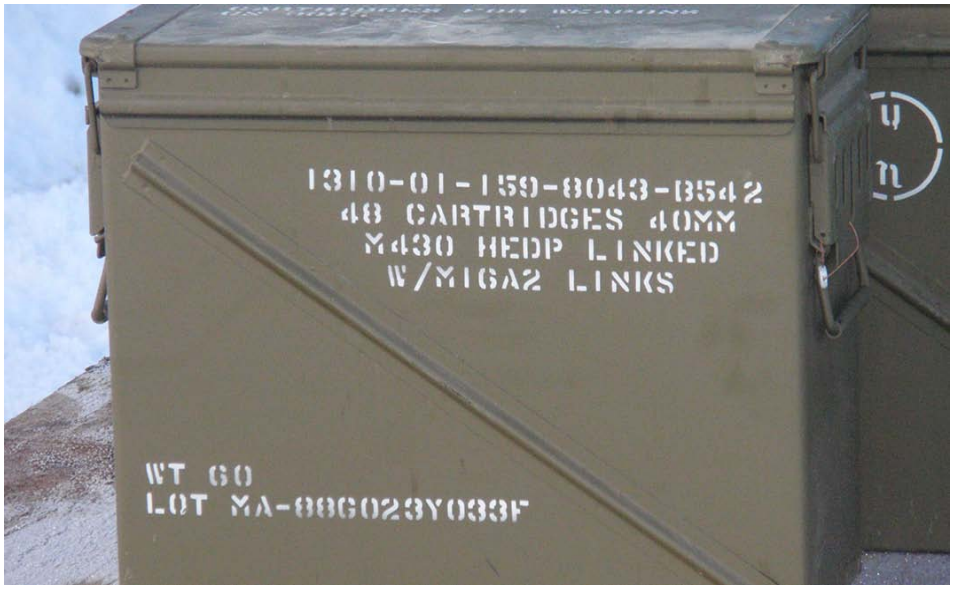

Figure A-2. Ammunition box for HE rounds used during test.

Appendix B: Analytical Results

Table B-1 contains sampling data for the test conducted on snow at the 40MM/AT4 (40/90) Range at Fort Richardson on 22-23 February 2010. Tables B-2 and B-3 contain the results of the analyses.

Table B-1. 40-mm firing point sampling data.

Sample ID Number	Scoop Size (cm X cm)	Sample Description	Number of Increments	Samplers	Sampled Area (m^2)	Notes
FRA10-01	10 X 10	Background Sample	30	SB/KLF	0.30	Entrance road
FRA10-02	10 X 10	Pad 1 (TP) 9 to 11.5 m	40	SB/JH	0.40	
FRA10-03	10 X 10	Pad 1 (TP) 9 to 11.5 m	40	SB/JH	0.40	
FRA10-04	10 X 10	Pad 1 (TP) 9 to 11.5 m	40	SB/JH	0.40	
FRA10-05	10 X 10	Pad 1 (TP) 5 to 9 m	40	MRW/AG	0.40	
FRA10-06	10 X 10	Pad 1 (TP) 5 to 9 m	40	MRW/AG	0.40	
FRA10-07	10 X 10	Pad 1 (TP) 5 to 9 m	40	MRW/AG	0.40	
FRA10-08	10 X 10	Pad 1 (TP) 0 to 5 m	40	MEW/KLF	0.40	
FRA10-09	10 X 10	Pad 1 (TP) 0 to 5 m	40	MEW/KLF	0.40	
FRA10-10	10 X 10	Pad 1 (TP) 0 to 5 m	40	MEW/KLF	0.40	
FRA10-11		Lab Filtration Blank				
FRA10-12	20 X 20	Pad 1 (TP) 0 to 5 m	38	MRW/AG	1.52	Larger scoop
FRA10-13	15 X 15	Baseline –Pad 2 mine	20	MEW	0.45	
FRA10-14	15 X 15	Baseline – Pad 2 mine	20	MEW	0.45	
FRA10-15	15 X 15	Background – Near FP	20	MEW	0.45	
FRA10-16	15 X 15	Background – End of lot	20	MEW	0.45	
FRA10-17	10 X 10	Pad 2 (HE) 10 to 13.5 m	40	SRB/JH	0.40	
FRA10-18	10 X 10	Pad 2 (HE) 10 to 13.5 m	40	SRB/JH	0.40	Triplicate SPE
FRA10-19	10 X 10	Pad 2 (HE) 10 to 13.5 m	40	SRB/JH	0.40	
FRA10-20	10 X 10	Pad 2 (HE) 5 to 10 m	48	MRW/AG	0.48	Triplicate SPE
FRA10-21	10 X 10	Pad 2 (HE) 5 to 10 m	48	MRW/AG	0.48	
FRA10-22		Lab Filtration Blank				
FRA10-23	10 X 10	Pad 2 (HE) 5 to 10 m	48	MRW/AG	0.48	
FRA10-24	10 X 10	Pad 2 (HE) 0 to 5 m	41	MEW/KLF	0.41	
FRA10-25	10 X 10	Pad 2 (HE) 0 to 5 m	42	MEW/KLF	0.42	
FRA10-26	10 X 10	Pad 2 (HE) 0 to 5 m	40	MEW/KLF	0.40	Triplicate SPE
FRA10-27	20 X 20	Pad 2 (HE) 0 to 5 m	48	MRW/AG	1.92	Larger scoop
FRA10-28		Lab Filtration Blank				

Table B2. Sample analytical results (NG) for 40-mm firing positions

Sample	NG Mass in Sample					NG Mass in Test Areas	
	Filtrate Portion			*Filter Portion*			
ID Number	Total (mg/L)	Total (mg)	Calculated (mg/m²)	Total (mg)	Calculated (mg/m²)	Total (mg)	Average (mg)
FRA10-01	-ND-	–	–	–	–	–	–
FRA10-02	-ND-	–	–	0.0020	0.005	0.11	
FRA10-03	-ND-	–	–	0.0050	0.013	0.26	
FRA10-04	-ND-	–	–	0.0020	0.005	0.11	0.16
FRA10-05	0.0024	0.0067	0.017	0.30	0.75	22	
FRA10-06	0.0014	0.0046	0.011	0.29	0.73	21	
FRA10-07	0.0017	0.0061	0.015	0.30	0.75	22	22
FRA10-08	0.021	0.0549	0.14	2.8	7.0	260	
FRA10-09	0.021	0.0525	0.13	2.7	6.7	250	
FRA10-10	0.025	0.0582	0.15	2.7	6.7	250	250
FRA10-11	-ND-	–	–	–	–	–	–
FRA10-12	0.017	0.21	0.14	12	7.8	290	290
FRA10-13	-ND-	–	–	–	–	–	–
FRA10-14	-ND-	–	–	–	–	–	–
FRA10-15	-ND-	–	–	–	–	–	–
FRA10-16	-ND-	–	–	–	–	–	–
FRA10-17	0.0025	0.0091	0.023	0.049	0.12	4.6	
FRA10-18	0.0017	0.0061	0.015	0.036	0.091	3.4	
(Triplicate)	0.0016	0.0056	–	–	–	–	–
(Triplicate)	0.0017	0.0062	–	–	–	–	–
FRA10-19	0.0033	0.011	0.028	0.039	0.10	4.1	4.0
FRA10-20	0.0044	0.021	0.043	1.9	3.9	160	
(Triplicate)	0.0044	0.020	–	–	–	–	–
(Triplicate)	0.0044	0.020	–	–	–	–	–
FRA10-21	0.0037	0.016	0.033	1.2	2.4	100	
FRA10-22	-ND-	–	–	–	–	–	–
FRA10-23	0.0051	0.023	0.047	3.0	6.2	250	170
FRA10-24	0.60	1.4	3.4	120	290	11000	
FRA10-25	0.58	1.4	3.2	110	260	10000	
FRA10-26	0.68	1.4	3.6	120	300	11000	11000
(Triplicate)	0.66	1.4	–	–	–	–	–
(Triplicate)	0.69	1.5	–	–	–	–	–
FRA10-27	0.24	3.2	1.7	350	180	7000	7000
FRA10-28	-ND-	–	–	–	–	–	–

Table B3. Sample analytical results (Akardite II®) for 40-mm firing positions.

Sample	Akardite II Mass in Sample					Akardite II Mass in test Area	
	Filtrate Portion			*Filter Portion*			
ID Number	Total (mg/L)	Total (mg)	Calculated (mg/m2)	Total (mg)	Calculated (mg/m2)	Total (mg)	Average (mg)
FRA10-01	-ND-	–	–	-ND-	–	–	–
FRA10-02	-ND-	–	–	-ND-			
FRA10-03	-ND-	–	–	-ND-			
FRA10-04	-ND-	–	–	-ND-			
FRA10-05	0.06	0.2	0.4	1.0	2.6	87	
FRA10-06	0.04	0.1	0.3	0.85	2.1	70	
FRA10-07	0.04	0.1	0.4	1.0	2.5	83	80
FRA10-08	0.51	1.3	3.3	9.4	24	978	
FRA10-09	0.52	1.3	3.2	8.8	22	913	
FRA10-10	0.58	1.4	3.4	9.0	23	948	946
FRA10-11	-ND-	–	–	–	–	–	–
FRA10-12	0.43	5.3	3.5	35	23	955	

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14. ABSTRACT

Military live-fire training utilizes energetic materials that are never completely consumed. In February 2010, tests were conducted at Fort Richardson, Alaska, to determine the propellant residues deposition rates related to the firing of 40-mm grenades from an Mk19 machine gun. Two test pads were constructed, with 127 Mk281 (BA12) training rounds containing F15080 propellant (10% nitroglycerin - NG) fired over one and 144 M430 (B542) high-explosive rounds containing M2 propellant (20% NG) fired over the other. Replicate multi-increment samples were collected from the snow surface downrange of the firing positions in three sampling units on each pad. Samples were analyzed and results composited to derive an estimate of the unreacted energetics mass. The total estimated per-round deposition rate for the M430 high-explosive cartridge is 76 mg/round, 8.4% of the original NG load. The deposition rate for the Mk281 cartridge is 2.2 mg/round, 0.59% of the original NG load. Energetics deposition rates for the M430 rounds were between those for mortar projectiles and shoulder-fired rockets, which also utilize double-based propellants, are medium-velocity projectiles, and are fired from short-barreled guns. The Mk281 cartridges, with their NG-impregnated propellant grains, had a much lower NG deposition rate but a greater mass of unconsumed propellant.

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